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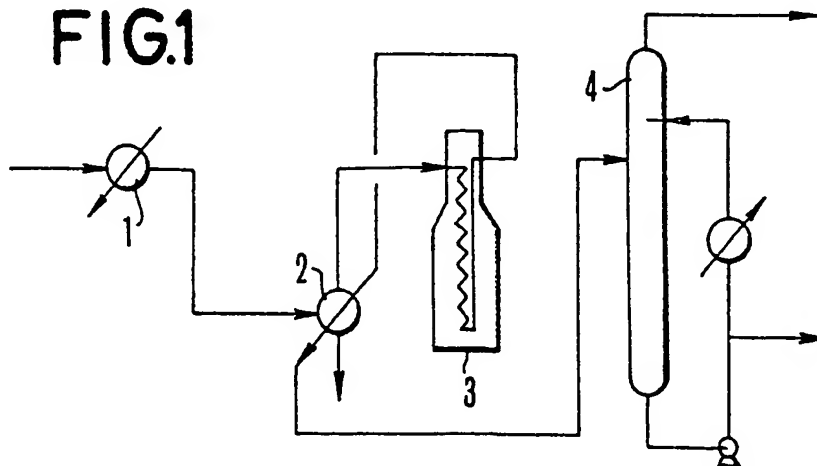
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Process for producing vinylchloride monomer by pyrolysis of 1,2-dichloroethane.

Process for producing vinylchloride monomer by pyrolysis of 1,2-dichloroethane comprising carrying out heat exchange between a high temperature cracked gas produced as a result of the pyrolysis and flowing out of a pyrolysis furnace and the 1,2-dichloroethane to be introduced in the pyrolysis furnace with a flow rate of the cracked gas at 5 m/s or more but less than 20 m/s until the cracked gas is cooled down to 180 - 350°C and introducing the 1,2-dichloroethane in the furnace for the pyrolysis.

FIG.1



PROCESS FOR PRODUCING VINYLCHLORIDE MONOMER BY PYROLYSIS OF 1, 2-DICHLOROETHANE

Background of the Invention:

Field of the Invention:

The present invention relates to a process for producing vinylchloride monomer (hereinafter designated as VCM) by the pyrolysis of 1,2-dichloroethane (hereinafter designated as EDC) under a pressure.

Description of the Related Art:

Previous art teaches for the production of VCM that purified EDC in a liquid form is introduced in a preheated zone of the pyrolysis furnace under a pressure and, after being evaporated in an evaporation zone, is thermally decomposed in a temperature range from 480 to 550°C in a pyrolysis reaction zone, to produce VCM.

In this treatment the cracked gas at a high temperature which flows out of the pyrolysis furnace mostly contains VCM and hydrogen chloride produced by the pyrolysis and the EDC remaining indecomposed. Usually the abundant heat of the cracked gas at a high temperature is exhausted away from the system with cooling water in a quencher which follows in the operation line. In the next step of operation, hydrogen chloride and the EDC remaining indecomposed are separated from VCM by use of a distillation column.

While the high temperature pyrolysis furnace for EDC is operated for a long period of time, rigid coke is formed generally in the inside of tube line. Therefore it is necessary to stop the operation before the pressure loss of the pyrolysis furnace itself exceeds the tolerance limit and decoke.

The rate of pyrolysis of EDC, or the yield of VCM per unit amount of EDC introduced in the pyrolysis furnace, can be enhanced by elevating the temperature at which the pyrolysis reaction takes place. As a result of the treatment, however, by-products such as methylchloride and butadiene which may cause trouble in polymerization are also increased. These by-products require a large amount of energy to be removed in the following stage.

Further, in the pyrolysis furnace where EDC is preheated, evaporated and decomposed by heat, the elevated temperature inside the furnace promotes the formation of rigid coke on the inside wall of tubes, which consequently shortens the life of the pyrolysis furnace.

In addition, the elevated temperature at which

the exhaust gas after combustion is exhausted from the pyrolysis furnace brings about a large increase in the loss of thermal energy.

For these reasons, temperature of the pyrolysis reaction of EDC in the actual operations is limited by the amounts of by-products and coke which may be formed in parallel. In other words, the rate of pyrolysis can hardly be increased beyond a certain level.

For reducing the amount of coking formed in the tubes of the pyrolysis furnace, Japanese Laid-Open Patent Application No. Sho 49-125306 proposes a process in which EDC is evaporated at the outside of the pyrolysis furnace or, in other words, gaseous EDC is introduced in the pyrolysis furnace.

In this process, however, requires a high temperature heat source for the evaporation of EDC and therefore a heating furnace for EDC is needed in addition to the pyrolysis furnace.

Further, additional problems of the heating furnace itself are deterioration of EDC due to the high temperature and necessity for removing the scales. Thus, the expense for the operation and equipment are necessarily a loss in the cost.

On the other hand, the cracked gas flowing out of the pyrolysis furnace holds in itself a tremendous amount of heat energy, so that the tremendous heat energy is lost in cooling water in a quencher located immediately after the pyrolysis furnace.

Therefore, a variety of methods have been proposed for recovering and utilizing the energy of the high temperature cracked gas flowing out of the pyrolysis furnace.

For instance, Japanese Laid-Open Patent Application No. Sho 56-45424 describes a method in which a cracked gas flowing out of a pyrolysis furnace is cooled at least in two steps and the heat transferred to a heat transfer medium is used for the purpose to heat other devices.

The heat transfer medium should be selected on consideration of resistance against the high temperature deterioration and the specific property of the gas flowing out of the pyrolysis furnace, that is to fear in the worst case explosion on leakage due to hydrogen chloride or others contained in the gas.

In particular, when water or steam is used as heat transfer medium, leakage of hydrogen chloride may probably cause severe corrosion and even breakage of devices.

In this case, the apparatus should be reconstructed into that of a larger scale, to utilize thus recovered heat.

Japanese Laid-Open Patent Application No. Sho 55-129233 discloses a process in which heat of a cracked gas is indirectly exchanged using a heat transfer medium and the heat transfer medium is employed as a heat source of a distillation column for EDC, as an example of using the heat transfer medium for a heat source in other operation.

Here, troublesome operation are usually required, for example, because the distillation column is under influence of the variation in the running conditions of the pyrolysis furnace. Furthermore, since usually a pyrolysis furnace is situated some distance apart from a distillation column, this operation above necessarily requires a large expense for the equipment.

Furthermore, another process is also proposed in which the exchange of heat between a cracked gas flowing from a pyrolysis furnace and EDC supplied to the pyrolysis furnace is utilized to preheat or evaporate the EDC.

In this case, however, the cracked gas flows out at a relatively high rate and therefore a fairly large length is necessary for the heat transmission tube of the heat exchanger. Consequently the pressure drop in the tubes results with the heat exchanger which is located immediately after the pyrolysis furnace and this entails to shorten the time for a continuous operation of the pyrolysis furnace. Thus, to overcome the difficulties, a large scale remodeling of the pyrolysis furnace is necessary, for example, to expand the diameter or shorten the length of the heat transmission tubes.

In order to raise the rate of pyrolysis without elevating the temperature of the pyrolysis reaction, or in other words without causing to increase the amount of by-products formed in the pyrolysis furnace and a loss in thermal energy, it is necessary to increase the area of reaction zone in the pyrolysis furnace without making any drastic remodeling of the furnace. Also for the reduction of coking in tubes of the pyrolysis furnace, gaseous EDC should be introduced in the pyrolysis furnace at a site which lies in a range of zones called for liquid EDC from the preheating zone to the evaporation zone, preferably at the entrance of the preheating zone.

The cracked gas flowing out of the pyrolysis furnace contains a large amount of thermal energy which is to be recovered by exchanging heat between the cracked gas and supplied EDC and be utilized for preheating and evaporating the EDC.

However, the mentioned task requires an effective heat exchanger which is installed immediately after the pyrolysis furnace and performs the exchange of heat between the cracked gas and supplied EDC with an operational condition set so as to minimize the pressure drop.

Further it is also necessary for a long during operation to prevent the continuous operation of the pyrolysis furnace from being interrupted by lowered capacity of the heat exchanger, increased pressure drop, and blocking of the heat exchanger due to scaling.

Summary of the Invention:

Under the circumstances mentioned above, the present inventors investigated how to minimize the pressure drop of the heat exchanger in which EDC introduced in the pyrolysis furnace is preheated and evaporated by the heat exchanged from the cracked gas at a high temperature and to reduce the amount of coke to be formed and be attached onto the heat exchanger while the device being operated. They found to obtain a good result when the exchange of heat between the high temperature cracked gas obtained from the pyrolysis in the furnace and the EDC to be introduced in the pyrolysis furnace is carried out until the cracked gas is cooled down to 180 - 350°C and with a flow rate of the same gas being equal to or more than 5 m/s but less than 20 m/s, followed by introduction of the EDC in the pyrolysis furnace to perform the pyrolysis. Thus, the present invention has been completed.

Detailed Description of the Invention:

The present invention will be explained in further details.

More particularly, the exchange of heat between a high temperature cracked gas from the pyrolysis furnace and EDC to be introduced in the pyrolysis furnace may be performed in any process, but preferably the heat exchanger is so designed that the gas is forced to flow in heat transmitting tube and the tube is immersed in the incoming liquid EDC.

The procedure mentioned above is preferably conducted with a flow rate of cracked gas ranging from 5 m/s to less than 20 m/s.

In case the flow rate of the cracked gas is less than 5 m/s, scaling mainly of carbon is accelerated on the inside wall of the tube, which adversely affects the heat exchanger and in the worst case the device may become inoperable on account of blockage of the tube.

When the flow rate of the cracked gas is 20 m/s or higher, pressure drop in the tube which is caused by the high rate of flow should be taken into consideration.

As far as the above conditions are satisfied, any type of a heat exchanger may be employed,

but preferably the heat exchanger be of a so-called mono-tube type.

Further the cracked gas should be preferably cooled down to 180 - 350°C. If the gas is cooled to a temperature below 180°C, unwanted condensation and a lowered rate of flow of the gas are feared at the lower temperatures, which may eventually cause to completely block the tube. On the other hand, if the gas is cooled down only to above 350°C, insufficient heat is recovered from the high temperature cracked gas and therefore an additional heat should be supplied for evaporation of EDC by means of steam or other source of heating. This brings about an economical disadvantage.

Liquid EDC to be supplied to the heat exchanger and to be eventually decomposed should be at a temperature between 160°C and 250°C.

If a temperature of the EDC below 160°C is undesirable, because it may be possible that the cracked gas is cooled down to below 180°C and this is to be avoided as mentioned above.

The exchange of heat which performs cooling of a cracked gas and preheating and evaporation of EDC to be supplied to the pyrolysis furnace can be carried out with a single heat exchanger. However, as far as the above conditions are met, the same object can be attained with plural separate devices, one is a heat exchanger which mostly preheats the EDC and the others are two or more heat exchangers which mostly contribute to evaporation of the EDC.

The gaseous EDC flowing out of the heat exchanger is taken care of so that it does not contain much mist or tiny drops of liquid EDC. It is introduced in the pyrolysis furnace at the site which ranges from the preheating to the evaporating zone, preferably at the preheating zone, for liquid EDC.

In this manner, the gaseous EDC as it is can be introduced in the pyrolysis furnace without making any change or with a slight change on the previous pyrolysis furnace, to permit the reaction zone to be enlarged in the pyrolysis furnace.

The enlarged area of zone described above for the pyrolysis reaction enabled the rate of pyrolysis of EDC or, in other words, the amount of VCM produced per unit amount of EDC supplied to be increased by approximately 5 - 10 % without any increase in the amount of unwanted by-products, any elevation of temperature after combustion of an exhaust gas from the pyrolysis furnace, and any consequent increase of loss in thermal energy.

Further, the amount of coke produced, or concurrent pressure drop, in the pyrolysis furnace was also decreased to 70 - 90 % as low as compared with the case when EDC in the liquid form was introduced in the pyrolysis furnace.

It was amazing to find that, after a long time

operation of the heat exchanger to evaporate liquid EDC, decrease in the purity of the EDC remaining in the heat exchanger was negligibly small and the gaseous EDC introduced in the pyrolysis furnace was as pure as the liquid EDC supplied to the heat exchanger.

This fact can be markedly observed when a part, or more particularly 5 - 10 %, of liquid EDC supplied to the heat exchanger is extracted as it is from the bottom of the heat exchanger and 95 - 90 % is evaporated and introduced in the pyrolysis furnace.

Even after a long time operation, no decrease in the purity was observed with the EDC remaining in the heat exchanger and the gaseous EDC to be introduced in the pyrolysis furnace.

In the heat exchanger in which exchange of heat was being carried out between EDC to be supplied to the pyrolysis furnace and a high temperature cracked gas flowing out of the pyrolysis furnace, it was feared at the part of the device where EDC was being evaporated that coking may cause to decrease the heat transmission and further disturb the operation. But surprisingly no bad influence was observed even if scales were formed. They might be readily peeled off so as not to disturb the operation.

Brief Explanation of the Drawings:

Figs. 1 and 2 are flow sheets of apparatus according to the process of the present invention and Fig. 3 is a flow sheet of an apparatus according to the process in Comparison Example.

Description of the Preferred Embodiments:

The present invention will be explained using some Examples, but the invention shall not be limited to them.

In this specification, pressures are expressed by the pressure on gauge and percentages (%) for proportions are by weight, if not otherwise specified.

Example 1

Employing an apparatus shown in Fig. 1, a single heat exchanger 2 served to cool a high temperature cracked gas from a pyrolysis furnace 3 and to preheat and evaporate EDC to be introduced in the pyrolysis furnace 3.

In this treatment, 8,600 kg/hr of liquid EDC being under a pressure of 36 atm was preheated up to 190°C in a heat exchanger 1 and supplied to

the bottom of the heat exchanger 2.

On the other hand, a cracked gas flowing out of the pyrolysis furnace 3, being 8,600 kg/hr, 500°C and 23 atm, was delivered at a flow rate of 9.2 - 13.8 m/s into the tube-side of the heat exchanger 2, to exchange heat with the fresh EDC.

Through the procedure above, the cracked gas leaving the heat exchanger 2 was at 245°C and further cooled to 80°C in the quencher 4 before being lead to next step of operation.

Total amount of the EDC supplied was evaporated and turned into a vapor at 265°C, which was then delivered to the pyrolysis furnace 3 at the part previously called preheating zone, so as to be decomposed thermally.

The cracked gas contained 3,200 kg/hr of VCM and also butadiene and methylchloride in amounts of 4.3 and 35 ppm by weight, respectively, per unit VCM. After a continuous operation for 95 days conducted under the above-mentioned condition, the increase in the pressure drop of the pyrolysis furnace 4 was 1.3 times as much owing to the coking in the inside of tubes of the pyrolysis furnace 4.

Further, the scales of which carbon molecule was the main ingredient were formed on the outer surface of the tube in the heat exchanger 2 with which the liquid EDC contacted, but most of the scales were peeled off. A small amount of coking could be found attached to the inside of the tube at the inlet part. The cracked gas made contact with the whole inside wall of the tube, but the metal surface remained uncoated except only at the inlet part. The capacity of operation was lowered by not more than 10 % of the original one and therefore no obstacle was observed for the operation.

The expenditure of energy from the heat exchanger 1 through the pyrolysis furnace 3 amounted to 71 % of that estimated in Comparison Example 1 of this specification.

Example 2

Following procedure was carried out using the apparatus shown in Fig. 2.

Liquid EDC in an amount of 8,600 kg/hr under an applied pressure 36 atm was preheated to 160°C with steam in a heat exchanger 1 and then lead to a heat exchanger 2 through which flowed 8,600 kg/hr of a cracked gas of 235°C coming from the pyrolysis furnace 3 through a heat exchanger 5 for the first step cooling.

The whole amount of liquid EDC cooled to 190°C in the heat exchanger 2 was further introduced in the bottom of the heat exchanger 5.

The cracked gas which suffered from the second cooling in the heat exchanger 2 was at a

temperature of 210°C and this was lead to a conventional quencher 4 to be cooled to 80°C.

Flow rate of the cracked gas was controlled in a range from 8.3 to 13.8 m/s in the heat exchanger.

The EDC introduced in the heat exchanger 5 experienced exchange of heat with the cracked gas of 500°C and 23 atm and was evaporated into a vapor of 265°C. This was then transferred to the pyrolysis furnace 3 at the site of preheating zone as called in convention processes, to perform the pyrolysis.

In this process 3,170 kg/hr of VCM could be obtained in the pyrolysis furnace 3 which contained 3.6 and 32 ppm by weight of butadiene and methylchloride, respectively, per unit VCM.

Expensive fuel supplied to the pyrolysis furnace 3 was 67 % as much as that appearing in Comparison Example 1 of this specification. After a continuous operation for about 70 days conducted under the same condition, increase in the pressure drop in the pyrolysis furnace 3 due to the coke which deposited on the inside wall of tubes in the pyrolysis furnace 3 proved to be approximately 1.3 times as much.

Further, the scales of which carbon molecule was the main ingredient were formed on the outer surface of the tube in the heat exchangers 2 and 5 with which the liquid EDC contacted, but most of the scales were peeled off. A small amount of coking could be found attached to the inside of the tube at the inlet part. The cracked gas made contact with the whole inside wall of the tube, but the metal surface remained uncoated except only at the inlet part. The capacity of operation was lowered by not more than 10 % of the original one and therefore no obstacle was observed for the operation.

After a 70 day operation, the liquid EDC remaining in the heat exchanger 5 which was concerned mainly with the evaporation of EDC changed its own concentration by 0.5 % as lower as that of the originally supplied EDC, but only a negligible influence was observed on the pyrolysis reaction.

Comparison Example 1

Decomposition of EDC was carried out using an apparatus shown in Fig. 3.

Liquid EDC in an amount of 8,600 kg/hr was preheated to 160°C with steam in a heat exchanger 1 under an applied pressure of 33 atm and delivered as it was in the liquid form to a pyrolysis furnace 3 at the preheating zone for EDC.

In this manner, the liquid EDC supplied was heated to about 260°C in the tube of the pyrolysis furnace 3 and then completely evaporated in the

evaporation zone and further incompletely decomposed by heat in the pyrolysis reaction zone.

The gas produced by the pyrolysis reaction was at a temperature of 510°C just after the pyrolysis. This was directly lead to a quencher 4 and cooled there to a temperature of 80°C before transferred to the next step of operation.

The gas produced by the pyrolysis reaction contained 2,960 kg/hr of VCM and further butadiene and methylchloride in amounts of 6 and 40 ppm by weight. respectively, per unit VCM.

After a continuous operation for 82 days under the same condition, rigid coke was formed and attached to the inside of the tube of the pyrolysis furnace 3, which lead to about 1.5 times as much pressure drop as that at the original stage with the pyrolysis furnace 3.

Claims

Process for producing vinylchloride monomer by pyrolysis of 1,2-dichloroethane comprising carrying out heat exchange between a high temperature cracked gas produced as a result of the pyrolysis and flowing out of a pyrolysis furnace and the 1,2-dichloroethane to be introduced in the pyrolysis furnace with a flow rate of said cracked gas at 5 m/s or more but less than 20 m/s until said cracked gas is cooled down to 180 - 350°C and introducing said 1,2-dichloroethane in the furnace for the pyrolysis.

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FIG.1

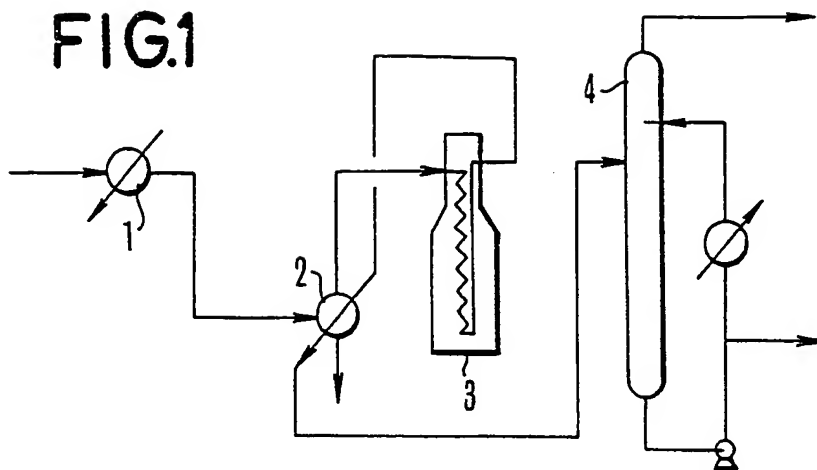


FIG.2

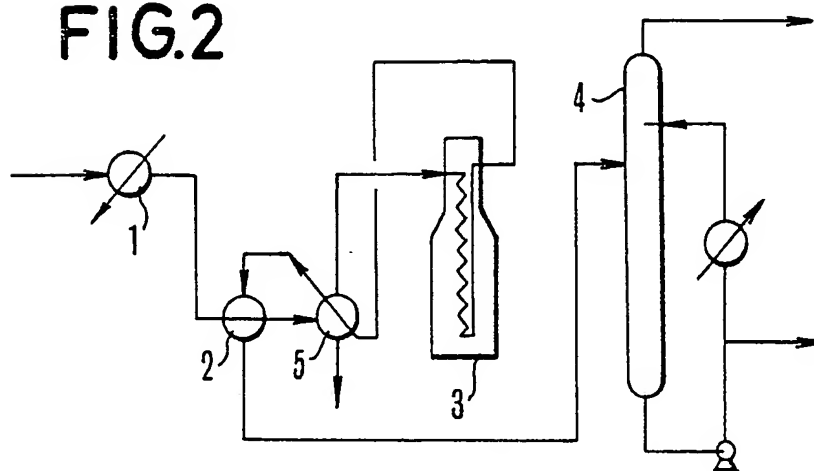


FIG.3

